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V S. Robinson
School of Mechnical Engineering, Purdue University

Timothy Fisher
Birck Nanotechnology Center and School of Mechanical Engineering, Purdue University, tsfisher@purdue.edu

J. A. Michel
Vanderbilt University

C. M. Lukehart
Vanderbilt University

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V. S. Robinson and T. S. Fisher[a)]
Purdue University School of Mechanical Engineering, and Birck Nanotechnology Center, West Lafayette, Indiana 47907

J. A. Michel and C. M. Lukehart
Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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Materials with low work functions hold great potential for improving the performance of thermionic energy converters and other thermionic emission devices. Thermionic electron energy distributions (TEEDs) of graphitic carbon nanofibers (GCNFs) with and without intercalated potassium are used to characterize performance under realistic operating conditions. TEEDs of intercalated GCNFs at temperatures of 600 and 700 °C reveal an effective work function of 2.2 eV, a reduction of 2.5 eV from the work function of the GCNF without intercalate. In addition, consistent with other published work, a narrowing of the electron energy spectrum's width occurs with intercalation. This narrower energy distribution may indicate emission from hybridized carbon–potassium states. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2009052]

Devices that employ thermionic emission are used in many contemporary applications that require a stable electron source. These applications include fluorescent lighting, cathode ray tubes, x-ray tubes, mass spectrometers, vacuum gauges, scanning electron microscopes, and other scientific instruments. Further, thermionic emission is also a viable means of converting heat directly into electrical power. Thermionic converters have been designed to operate in conjunction with various heat sources such as solar radiation, nuclear reactions, and the combustion of fossil fuels. Thermionic power generation has many attractive qualities, including compactness, scalability, and high waste heat rejection temperatures for cascaded systems.[1,2] However, the requirement of operation at high temperature caused by the high work functions of typical thermionic emitter materials has limited the applicability of thermionic power generation. The purpose of the work reported herein is to determine the effect of potassium intercalation on the work function of graphitic carbon nanofibers in a practical experiment at elevated temperatures.

Carbon nanotubes[3] and nanofibers[4] exhibit outstanding electron field emission properties because of electric field enhancement caused by their large geometric aspect ratios. As measured by photoelectron emission spectroscopy,[5] unmodified single- (SWCNTs) and multiwalled carbon nanotubes exhibit work functions of $\phi \approx 5$ eV that are slightly higher than graphite, and the work function of carbon nanofibers is expected to be similar. Suzuki *et al.*[6] first studied the effects of cesium intercalation on the work function of SWCNTs and measured by ultraviolet photoemission spectroscopy a work function of 2.4 eV for the intercalated sample as compared to 4.8 eV for pristine SWCNTs. Other alkali-metal intercalants have also been studied. Suzuki *et al.*[7] showed a reduction in work function from 4.6 eV to 3.2 eV in SWCNTs with the addition of potassium, and Choi *et al.*[8] measured a reduction in work function of up to 0.2 eV with sodium-intercalated multiwalled carbon nanotubes. In addition, potassium doping of SWCNTs has recently been reported to exhibit a strong effect on field effect transistor device characteristics.[9]

The observed reductions in work function indicate that carbon nanotubes and nanofibers may be useful thermionic emission sources. However, prior measurements have been conducted using photoemission at room temperature and have therefore not interrogated the stability of these materials under actual operating conditions. In the present work, we measure the energy distributions of electrons emitted thermionically from heated graphitic carbon nanofibers. The resulting measurements provide energy distributions from which insights involving work functions and energy levels can be ascertained.

The herringbone graphitic carbon nanofibers (GCNFs) used in this study were prepared according to published procedures[10] using a Fe–Cu (7:3) growth catalyst under a flow of $C_2H_4/H_2/He(2:1:4)$ at 600 °C for 1.5 h. GCNFs are formed from the catalytic decomposition of a carbonaceous gas at the surface of metal growth catalyst nanoparticles. Carbon extracted from the gaseous reagent traverses the growth catalyst particle and deposits on specific facets, forming a carbon nanofiber in a layer-by-layer growth process.[11] Rodriguez *et al.*[12] have shown that the structural form of the resulting nanofiber can be manipulated by varying the metal composition of the growth catalyst and/or the source of carbon. In the present work, GCNFs having a herringbone graphene plane stacking structure, shown in Fig. 1, have been used. This structure consists of nested graphene (or cuplike) layers canted at ~90° and stacked in the direction of the long nanofiber axis. Individual GCNFs have diameters determined by the size of the individual growth catalyst nanoparticles and lengths determined by the growth conditions. The graphene-plane stacking pattern of GCNFs is uniquely different from that of SWCNTs or multiwalled nanotubes. As-prepared nanofibers were demineralized by etching away the retained metal growth catalyst with 1 M HCl solution for seven days at room temperature. Demetallated GCNFs were then washed with water and dried to a black powder. Transmission electron microscopy (TEM) mi-

[a)]Author to whom correspondence should be addressed; electronic mail: tsfisher@purdue.edu

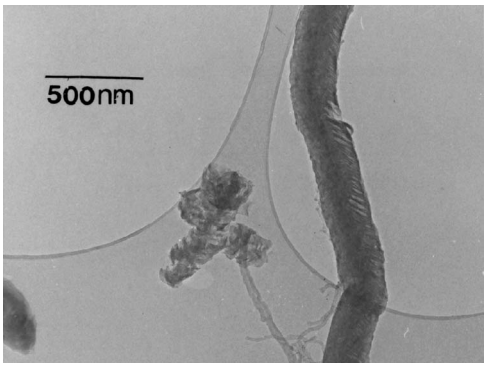

FIG. 1. TEM image of herringbone GCNFs showing canted graphene sheets stacked along the long nanofiber axis as grown from surface facets of a metal catalyst nanoparticle. Other representations for this GCNF structure include nested cuplike graphene layers in which nanofiber growth occurs from more than two canted crystal facets.

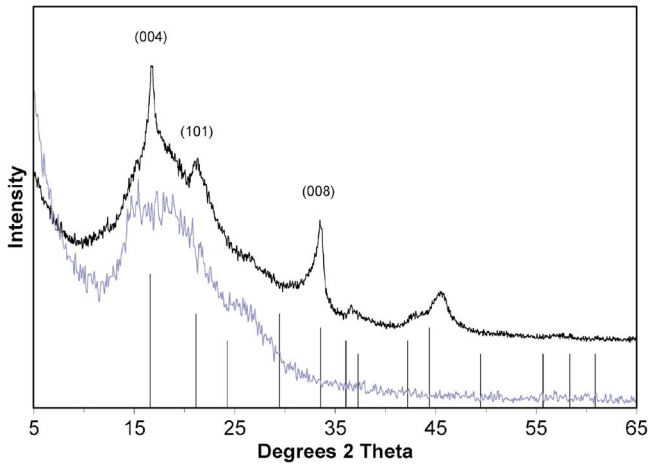

FIG. 2. (Color online) Powder XRD scan (Cu $K\alpha$ radiation) of a Stage-1 (KC_8) herringbone GCNF-potassium metal intercalate [top curve, peaks indexed to corresponding peaks of bulk KC_8 shown as a line pattern (JCPDS Card 04-0221)] recorded under a protective Kapton™ cover. An XRD scan typical of the Kapton™ cover film is shown as the bottom curve, and a slight sample-displacement offset is evident.

crographs confirm the herringbone structure of the GCNF product with nanofibers typically having diameters of 75–200 nm and lengths on the micron scale.[13]

A Stage-1 GCNF-K intercalate was prepared by direct reaction of herringbone GCNFs with the stoichiometric amount of molten potassium under a nitrogen atmosphere (MBraun glove box). A reaction temperature of 250 °C was maintained over 12 h. During reaction, the black GCNFs developed a bronze appearance, indicating formation of the desired intercalate.[14] Intercalated nanofibers were placed in an air-tight die within the glove box and pressed outside the glove box into pellets (13 mm × 2 mm), which were returned to the glove box, rinsed, and stored in decane. Upon removal from the decane, the GCNFs' appearance was again black and visually indistinguishable from the nonintercalated sample.

Thermionic energy distributions were measured with a hemispherical energy analyzer (SPECS-Phoibos 100 SCD) connected to a vacuum chamber that reaches pressures on the order of 10^{-8} Torr. When transferred into the vacuum chamber, the sample pellet was briefly exposed to atmospheric air, during which time no observable reaction occurred. The heated emitter sample was located at the focal plane, 40 mm below the analyzer's aperture. The analyzer nozzle, inside the vacuum chamber, was wrapped with copper cooling tubes to prevent heat damage. The temperature of the molybdenum heater (HeatWave Labs, Inc.) was measured by a K-type thermocouple (embedded 1 mm below the top of the molybdenum heater surface) that was connected to a proportional temperature controller. The uncertainty in the temperature measurements for the range of temperatures in this study (600–836 °C) is ±20 °C.

The heater assembly was thermally and electrically insulated from the chamber by alumina hardware. All energy distributions reported here were measured after the temperature of the emitter had stabilized for at least 20 min. The heater was negatively biased (−4 V) to accelerate electrons into the analyzer and to ensure that the electrons possessed sufficient energy to overcome the work function of the analyzer. Electron acceleration was achieved by connecting the heater assembly to a dc power supply (Hewlett Packard 6542A) and grounding the analyzer's aperture. Voltage sense lines for the dc power supply were implemented, reducing the uncertainty in the acceleration voltage to ±0.3 mV.

As found with a wide variety of graphitic carbon materials,[15] direct reaction of herringbone GCNFs with a stoichiometric amount of molten potassium metal gives a Stage-1 KC_8 potassium/GCNF intercalate. The resulting powder reacts rapidly upon exposure to ambient atmosphere and should be treated as a pyrophoric material (CAUTION). A powder x-ray diffraction (XRD) scan of an unpressed portion of the GCNF-K intercalate, protected from the atmosphere by a thin Kapton film, is shown in Fig. 2. Formation of the KC_8 stage is evident from the observed diffraction pattern. The expected (004), (101), and (008) diffraction peaks are clearly evident, and diffraction from the (002) planes at ~27° in 2θ normally observed for as-prepared GCNFs is absent. The (004) diffraction peak of bulk KC_8 is the peak of highest relative intensity and corresponds to the characteristic intercalate repeat distance of ca. 5.35 Å.

Figure 3 illustrates the effects of intercalating GCNFs with potassium on work function and thermionic electron energy distributions. Without intercalation, the peak intensity at $T=836$ °C occurs at 4.8 eV which, after accounting for the thermal energy kT, corresponds to an effective work function of approximately 4.7 eV. For the K-intercalate

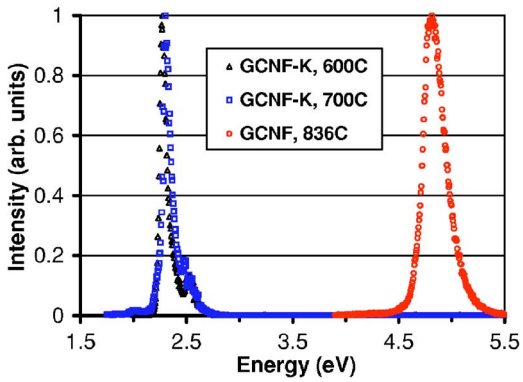

FIG. 3. (Color online) Normalized TEEDs for two types of GCNFs. Distributions produced by GCNFs with potassium intercalation at 600 °C (open triangles) and 700°C (open circles) indicate a work function of $\phi=2.2$ eV, while the distribution produced by the nonintercalated GCNF (open square) indicates a work function of $\phi=4.7$ eV.

sample tested at $T=600$ and 700 °C, peak intensities occur near 2.3 eV, corresponding to an effective work function of approximately 2.2 eV. Thus, intercalating GCNFs with potassium reduces the work function by approximately 2.5 eV. Further, the nature of the energy analyzer measurements suggests that this decrease is an aggregate effect over the entire sample surface and not limited to a local emission site, as indicated by the absence of a graphitic peak in the thermionic electron energy distributions (TEEDs) of the intercalated sample. For the intercalated samples, the effective work function is significantly smaller that that of graphite but similar to that of potassium, suggesting that the potassium dominates in the determination of effective work function. The difference between the work function reported here ($\phi=2.2$ eV) for GCNF-K and that reported by Suzuki *et al.*[7] ($\phi=3.2$ eV) for potassium-intercalated SWCNTs with a K/C ratio of approximately 0.14 (similar to that in the present work) may be the result of differences in intercalate position within the carbon lattice.

In addition to the the change in work function, Fig. 3 also shows a decrease in width of the energy distribution with intercalation, as quantified by the distributions' full width at half maximum (FWHM) intensity. The FWHMs are approximately 0.08 eV and 0.24 eV for the intercalated and nonintercalated samples, respectively. Part of the energy spread is attributable to instrument effects. The uncertainty associated with the energy analyzer is characterized by the standard deviation σ of a Gaussian instrument function which, when combined with the actual energy distribution, produces the observed energy distribution.[16] This function depends on instrument slit width and pass energy settings. For all reported cases, these settings were held constant and produced a σ value of approximately 0.008 eV.

Given that instrument effects were consistent for all experiments, the broader distribution for the nonintercalated sample is attributed, in part, to the slightly higher temperature, which was necessary to permit sufficient electron counts in the experiment. The maximum temperature difference among the experiments (236 °C), accounts for only 0.02 eV of the total 0.16 eV difference according to free-electron theory. Further, we note that free-electron theory predicts a FWHM of $2.45kT$,[17] which is remarkably consistent with the results for the nonintercalated GCNF ($2.45kT=0.234$ eV) but much larger than the observed FWHMs for the GCNF-K sample. The disparity in energy distribution widths thus cannot be explained by free-electron theory. A narrowing of the distribution in the room-temperature photoemission spectra of intercalated SWCNTs was also observed by Suzuki *et al.*,[7] who postulated that a hybridized state exists between the nearly free-electron (NFE) state of the SWCNT and an *s* state of the potassium. Because this NFE state corresponds to an interlayer state in graphite,[18] this argument would also apply to GCNFs. Nevertheless, detailed confirmation of this phenomenon remains to be reported.

In summary, TEEDs from GCNFs with and without potassium intercalation reveal a dramatic reduction in work function from 4.7 eV to 2.2 eV due to intercalation. This reduction is generally consistent with prior photoemission experiments on fibrous carbon materials with intercalated alkali metals, but an important difference is that the present results were performed at elevated temperatures. The results thus indicate that the effect can be maintained at high temperatures that would be required in applications of these materials as thermionic electron sources and energy conversion materials. Other features of the TEEDs involve a reduction in the width of the energy spectrum that may be the result of hybridized carbon–potassium states, and quantitative modeling of this phenomenon would serve to elucidate this issue.

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